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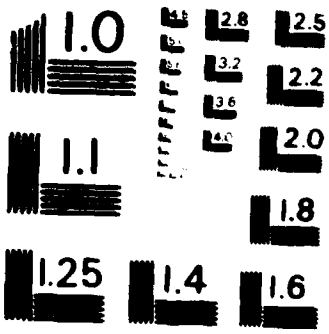
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19. ABSTRACT (Continue on reverse if necessary and identify by block number)

The main thrust of the research was the study of supercritical fluids as applied to chromatography and mass spectrometry. The most important results obtained were: (1) the ability to qualitatively predict and study the effects of solute retention using polar modifiers to enhance separations and decrease retention times; (2) the capability of rapid pressure programming in capillary SFC which greatly reduced separation times; (3) the continued evolution and improvement in design and implementation of SFC-MS, direct fluid injection-MS interfaces and capillary flow restrictors leading to enhanced detection capabilities; and (4) the understanding of the effects of fluid density on the enthalpy of solute transfer in SFC. These results have allowed the chemical tailoring of mobile phase interactions between the solvent and solute for enhanced separations. Most importantly the results on interface design in SFC-MS and DFI-MS allow these techniques to assume an important role in the

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20. ABSTRACT CONTINUED

characterization and analysis of thermally labile, nonvolatile components, which were formally intractable by other methods.

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FINAL REPORT

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PERIOD COVERED BY REPORT: Final Report October 1, 1983 - September 30, 1986.

TITLE OF PROPOSAL: Conduct Studies of Supercritical Fluids Relevant to Chromatography and Mass Spectrometry.

CONTRACT OR GRANT NUMBER: DAAG29-83-K-0172

NAME OF INSTITUTION: Battelle Northwest Laboratories

AUTHOR(S) OF REPORT: Clement R. Yonker and Richard D. Smith

FOREWARD:

Supercritical fluids or dense gases have shown themselves to be flexible solvents in extraction and separation processes. This flexibility is derived from a combination of physical properties. A supercritical fluid has mass transfer characteristics similar to a gas (low viscosities) and densities (solvent properties) similar to a liquid. Solvent strength of a supercritical fluid is a function of pressure and temperature. Both of these parameters are easily controlled, which leads to enhanced efficiency in extraction or separation processes for thermally labile and/or non-volatile systems.

The main thrust of research conducted under this grant was the study of supercritical fluids as applied to chromatography and mass spectrometry. Supercritical fluid chromatography (SFC) takes advantage of the established solvent strength-density relationship coupled with the enhanced mass transport properties of the fluid. Capillary SFC has demonstrated efficiencies greater than liquid chromatography with reduced separation times. The use of a supercritical fluid as the transport solvent for solute introduction into the ion source of a mass spectrometer takes advantage of lower solvent density and ease of solvent vaporization (many commonly used fluids are permanent gases at ambient conditions) facilitiating solute introduction into, and greater compatibility with, the high vacuum region in the ion source of the mass spectrometer. The

combination of supercritical fluid chromatography and mass spectrometry has produced a new analytical method which yields specific molecular information for many materials which are intractable by other methods. Thermally labile, and less volatile solutes have been demonstrated during the course of this work to be routinely analyzed by SFC-MS. The extension to higher molecular weight, non-volatile components is also feasible using binary fluid solvent systems that are chemically tailored for the specific application. Further effort is required in this area to extend SFC and SFC-MS to polar, non-volatile solutes, and a proposal has been submitted for such research.

Supercritical fluids applied to SFC and SFC-MS introduce novel solvent properties that are used to create enhanced solute separations and identification in these analytical methods. One goal of this program was to greatly extend the knowledge of possible fluid systems and elevate solvent selection to a more systematic level as well as provide for the necessary background to the development of capillary columns specifically designed for a range of supercritical fluid systems. The major tasks of this program involved: (1) the development of a rational scheme for fluid selection, particularly for more polar and hydrogen-bonding systems, based upon established fundamental and empirically-developed solubility relationships, (2) investigations relevant to the evaluation of the stationary phase and interfacial kinetics fundamental to the chromatographic process, and (3) the continued evolution and evaluation of direct fluid injection mass spectrometry and capillary SFC-MS.

The most important results obtained during this three-year period of study were: (1) the ability to qualitatively predict and study the effects of solute retention using polar modifiers to enhance separations and decrease retention times; (2) the capability of rapid pressure programming in capillary SFC which greatly reduced separation times; (3) the continued evolution and improvement in design and implementation of SFC-MS, direct fluid injection-MS interfaces and capillary flow restrictors leading to enhanced detection capabilities; and (4) the understanding of the

effects of fluid density on the enthalpy of solute transfer in SFC. These results have allowed the chemical tailoring of mobile phase interactions between the solvent and solute for enhanced separations. Most importantly the results on interface design in SFC-MS and DFI-MS allow these techniques to assume an important role in the characterization and analysis of thermally labile, non-volatile components, which were formally intractable by other methods. Detailed descriptions of these developments have been given in papers prepared for publication during the course of this program.

A list of manuscripts published during this proposal period is as follows:

B. W. Wright and R. D. Smith, "Investigation of Polar Modifiers in Carbon Dioxide for Capillary Supercritical Fluid Chromatography," J. Chromatogr. 355 (1986) 367-373.

B. W. Wright, H. T. Kalinoski and R. D. Smith, "Investigations of Retention and Selectivity Effects Using Various Mobile Phases in Capillary Supercritical Fluid Chromatography", Anal. Chem. 57 (1985) 2823-2829.

R. D. Smith, H. R. Udseth and B. W. Wright, "Micro-Scale Methods for Characterization of Supercritical Fluid Extraction and Fractionation Processes", Supercritical Fluid Technology, J. M. L. Penninger, M. Radosz, M. A. McHugh, V. J. Krukonis, Eds. Vol. 1, Elsevier (1985) 191-223.

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R. D. Smith, E. G. Chapman and B. W. Wright, "Pressure Programming in Supercritical Fluid Chromatography", Anal. Chem. 57 (1985) 2829-2836.

C R. Yonker and R. D. Smith, "Effect of Density on Enthalpy and Entropy of Transfer for Supercritical Fluid Chromatography", J. Chromatogr. 351 (1986) 211-218.

R. D. Smith, J. L. Fulton, R. C. Petersen, A. J. Kopriva and B. W. Wright, "Performance of Capillary Restrictors in Supercritical Fluid Chromatography with Gas Phase Detectors", Anal. Chem. 58 (1986) 2057-2064.

B. W. Wright, H. T. Kalinoski, H. R. Udseth and R. D. Smith, "Capillary Supercritical Fluid Chromatography-Mass Spectrometry", HRC &CC 9 (1986) 145-153.

C. R. Yonker R. W. Gale and R. D. Smith, "Solute Iostherms in Supercritical Fluid Chromatography", submitted to J. Chromatogr.

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Dr. Clement R. Yonker
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